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Electro-optical properties of ZnO : Al thin films produced by sol-gel route

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Abstract : Both undoped and aluminium doped ZnO thin films of high quality were prepared by sol-gel route on glass substrates. Zinc acetate and isopropyl alcohol were taken as precursor materials. The conditions for preparations were optimized. Aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$) was doping material for aluminium doping and Zn/Al ratio was varied in the solution to vary doping concentration in the film. Structural characterizations were performed by XRD and TEM studies. The optical and electrical properties of the films were studied in detail and they were correlated with the doping concentrations and preparations conditions. The films deposited at optimized conditions on glass substrates showed electrical conductivity ~1.39 $(\Omega\ cm)^{-1}$ and a transmission of about 90% in the visible region. Electrical properties were studied in detailed which indicated that the films showed activated electronic conduction and the activation energies were found to depend on the doping concentrations in the films. Room temperature Seebeck co-efficient was obtained –91.65 μV/K in optimized condition.

Keywards : Zinc oxide, sol-gel route, aluminium doping.

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1. Introduction

Transparent conducting oxides (TCO) are known during the last four decades and extensive researches have been done on these materials. Among these materials indium tin oxides (ITO) and zinc oxide (ZnO) are two most important semiconductors because of their excellent combinations of electrical and optical properties. ZnO films have several promising applications in solar cells [1], gas sensors [2], transducers [3], luminescent materials [4] *etc.* only to mention a few. Doped ZnO, especially ZnO : Al, have high temperature stability because the doping effect is not caused by oxygen deficit. They do not degrade active solar cell materials owing to interdiffusion of constituents as it occurs with ITO.

Zinc oxide films have been prepared by a wide variety of methods such as spray pyrolysis [5], metal organic chemical vapor deposition [6], reactive magnetron sputtering [7,8], ion assisted evaporation [9] and sol gel methods [10–12]. All these methods have their advantages and disadvantages and choice of any particular technological route is dictated by many conditions such as cost effectiveness, capability of the technique to coat a large area, quality and reproducibility of the methods. While the last two factors are generally better in sophisticated deposition techniques, such as magnetron sputtering or MOCVD than the sol-gel method, but the first two factors dictate that sol-gel process will be the only industrially viable process in future. There are not so many reports on the synthesis of ZnO thin films by sol-gel methods in the literature, and more research is necessary to improve the properties and reproducibility of the ZnO films by sol-gel process. In this paper we report synthesis and characterization of ZnO and ZnO : Al thin films by sol-gel method on glass and Si substrates.

2. Experimental procedure

Aluminium doped zinc-oxide (AZO) films were prepared on glass substrates from ($Al(NO_3)_3 \cdot 9H_2O$), ($Zn(CH_3COO)_2 \cdot 2H_2O$) and isopropyl alcohol (Pr^i-OH). Diethanolamine (DEA) was added to get transparent

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solutions due to low solubility of zinc acetate into the isopropyl alcohol. Initially ($Zn(CH_3COO)_2{\cdot}2H_2O$) and ($Al(NO_3)_3{\cdot}9H_2O$) were dissolved in isopropyl alcohol mixed with alkanolamine (DEA) and the resultant solution was stirred keeping the temperature fixed ~70°C for one hr. Distilled water (~5 ml) and small amount of acetic acid were added for better stable of the solution and avoid from geletion or precipitation. After stirring the solution, it was aged also for one hr. The percentage of atomic ratio of Al/Zn were varied from 0.32×10^{-2} to 1.62×10^{-2} in solution and the concentration of zinc acetate was fixed at 0.85 mol l^{-1}. Now the clean and ultrasonicated glass substrate was dipped into solution and withdrawn at a slow rate to coat it. The coated substrate was dried at room temperature for 10 minutes and heated at 250°C for 10 minutes in open atmosphere. This process was continued 3 to 5 times getting to desire thickness. Finally the film was heated at the same temperature for one hr.

X-ray diffractometer (Philips PW 1730/10) with Cu-K_α radiation was used for crystal structure determination. UV-visible spectrophotometer (Hitachi, U-3410) was used for the optical characterization. Scanning electron microscopy and transmission electron microscopy were carried out by (JEOL, JSM-5200) and (Hitachi, H-600) respectively. For conductivity measurements, standard four-probe method has been used with silver paste as Ohmic contact.

2. Results and discussions

3.1. X-ray diffraction analysis :

X-ray diffraction (XRD) pattern of an Al doped ZnO thin film deposited on glass substrates is shown in Figure 1. Most of the peaks are from (100), (002), (101), (102), (110), (103) and (112) reflections of hexagonal ZnO having $a = b = 3.249$ Å and $c = 5.205$ Å. Information on crystallite size (L) and strain (ε) obtained

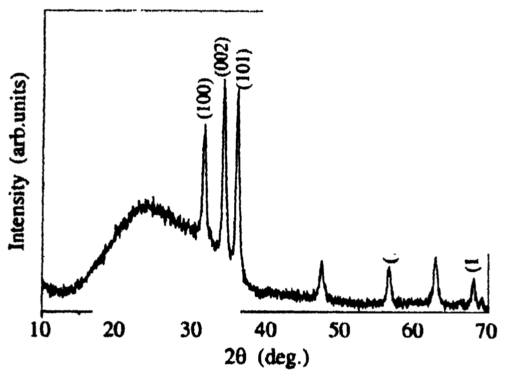

Figure 1. XRD pattern of ZnO : Al thin film for %Al = 0.65.

from XRD data are related by the following equation [13]

$$\frac{\beta\cos\theta}{\lambda} = \frac{1}{L} + \frac{\varepsilon\sin\theta}{\lambda}, \qquad (1)$$

where β is the fullwidth at half maxima (FWHM).

Figure 2 shows the plot of $\beta\cos\theta/\lambda$ *vs* $\sin\theta/\lambda$. From slope of the line and the intercept at $x = 0$ we calculated the strain (ϵ) and crystallite size (L) respectively. The

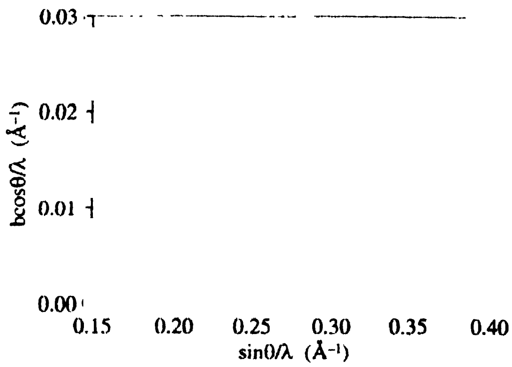

Figure 2. Graph for size-strain analysis.

crystallite size was found to be ~88.5 nm and the strain $\sim 5.82 \times 10^{-2}$. We have also confirmed from X-ray diffraction that there is no peak of Al even at higher percentage (1.96%) of Al.

3.2. SEM and TEM :

Surface morphology was studied by scanning electron microscope. Figure 3 shows the SEM micrograph of an Al doped ZnO thin film deposited by sol-gel process. Average grain size found from the SEM micrograph was ~0.12 μm. Cross sectional SEM measured the thickness of the film ~0.6 μm.

Also structural characterization was carried out by TEM studies. For TEM measurement, samples were prepared by dispersing the materials into methanol and copper grid was immersed into the ultrasonicated methanol

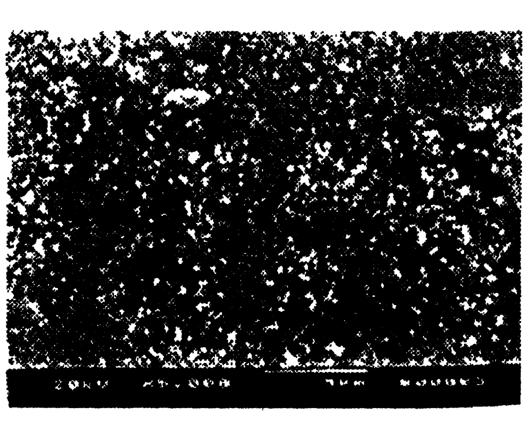

Figure 3. SEM micrograph of ZnO film.

solution. The diffraction pattern (not shown here) shows the characteristic spots with the lattice spacing (d) values of 2.81,2.25,1.91, 1.62 and 1.463 Å which correspond to the (100), (101), (102), (110) and (103) reflections respectively of hexagonal ZnO crystal.

3.3. *Optical properties :*

Al doped ZnO thin films have been used for their high conductivity and extensive transmission of visible light. The transmittance spectra of undoped and Al doped ZnO deposited on glass substrates has shown in Figure 4. From the transmittance data, using Manifacier model [14]

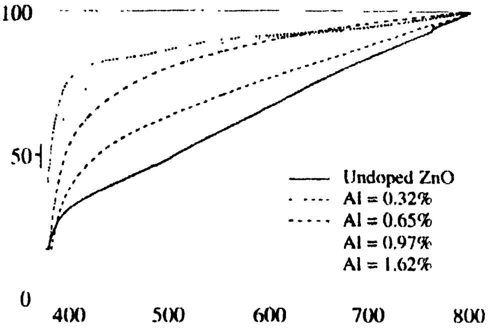

Figure 4. UV-vis transmittance spectra of ZnO : Al film for different Al cocentrations.

we have calculate absorption coefficients (α).at the region of strong absorption. Absorption coefficient (α) and photon energy ($h\nu$) are related by the formula [15]

$$(\alpha h\nu)^2 = A(h\nu - E_g), \quad (2)$$

where A is a constant and slope of this curve represents band gap energy (E_g) of this material.

We have observed that band gap energies has increased from 3.22 to 3.31 eV as the percentage of Al has increased from 0.32 to 1.62 respectively. These values are smaller than E_g of 3.35 eV found for bulk crystalline ZnO [16]. Inspite of small increase in band gap in Al doped ZnO films, its conductivity increases because the conduction electron obtained by ionization of the introduced donor levels dominate the electrical transport.

3.4. *Electrical properties :*

The temperature dependence of dc conductivity (σ) of Al doped ZnO films were measured by Keithley electrometer (Model 6514) in the temperature range 300–500 K. Figure 5 shows the lnσ *vs* 1000/T plots for different Al percentage. The conductivity can be expressed as in the simplest from,

$$\sigma = \sigma_0 \exp(-E_a/kT), \quad (3)$$

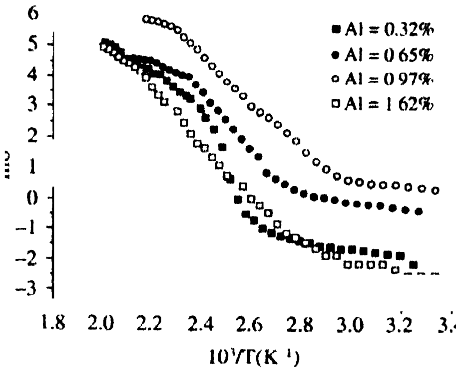

Figure 5. Temperature dependence of conductivity for different Al percentage.

where E_a is the activation energy, the minimum energy required to transfer electrons from donor level to conduction band, obtained from slope of the plots of lnσ *vs.* $10^3/T$. Comparative study of activation energy (E_a) and room temperature conductivity (σ_{RT}) are shown in Table 1 for different Al percentage. The activation (E_a) energies are different for different ranges of 1000/T but we have shown the values of activation energy in the Table 1, calculated from slope at middle portion of the plot.

Table 1. Comparative study of activation energy (E_a) and room temperature conductivity (σ_{RT}).

Sample no.	% Al	σ_{RT} $(\Omega\ \mathrm{cm})^{-1}$	E_a (meV)
ZO-42	0.32	0.12	1192
ZO-40	0.65	0.68	779
ZO-35	0.97	1.392	638
ZO-41	1.62	0.08	886

Undoped ZnO has smaller conductivity at room temperature and even at higher temperature (~600°K) [17] also. But Al doped ZnO has large conductivity at room and high (~500°K) temperature. Room temperature conductivity (σ_{RT}) increases from 0.12 to 1.39 $(\Omega\ \mathrm{cm})^{-1}$ whenever percentage of Al increases from 0.32 to 0.97 and further increase of Al (1.62%) percentage, decreases the conductivity to 0.08 $(\Omega\ \mathrm{cm.})^{-1}$. The increase in electrical conductivity brought in by the aluminium doping can be explained as follows : the concentration of free charge carriers in ZnO increases by the aluminium doping because aluminium has one valance electron more than zinc. We may consider that aluminium substitutes the zinc atom or it occupies interstitial sites. In both cases, aluminium acts as a donor. For higher percentage of Al doping, though the carrier concentration increases, due to much scattering of carriers, conductivity decreases. The main scattering mechanisms for charged carriers in thin films are lattice scattering, ionized impurities scattering and grain boundary scattering [18]. So optimum percentage of Al is 0.97 for getting highest conductivity at room temperature. It may be mentioned here, that in the optical transmission spectra, at the wavelength corresponding to the activation energy, some signature of absorption should also come. The maximum activation energy obtained by us was ~1.2 eV which corresponds to wavelength 1035 nm. This is beyond our measured spectral range as is evident from Figure 4.

Thermoelectric power measurements indicated negative value of Seebeck coefficient (S), thus confirmed n-type nature of the material. Seebeck coefficients were calculated from the derivatives of the thermoemf *vs* temperature difference plot (not shown here). Figure 6 shows the temperature variation of Seebeck coefficient for 0.97%Al

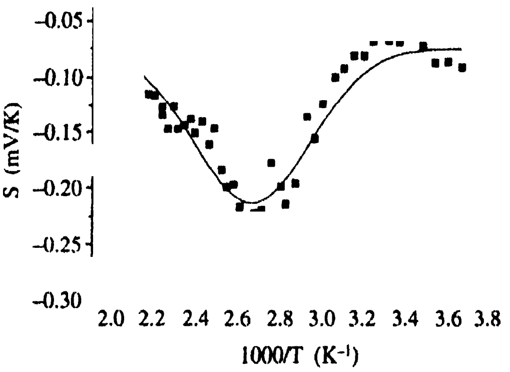

Figure 6. Seebeck coefficient *vs* temperature plot.

doped ZnO film. Value of room temperature Seebeck coefficient was found ~ -91.65 μV/K for 0.97% of Al.

4. Conclusions

Undoped and Al doped ZnO thin films were prepared by sol-gel processes. X-ray diffraction (XRD) pattern and selected area diffraction pattern confirm the hexagonal crystal structure of ZnO. Dopant Al slightly increases the bandgap from 3.20 to 3.31 eV. Maximum room temperature conductivity obtained was 1.39 (Ω cm)$^{-1}$. Thermoelectric power measurements confirm the material is n-type and Seebeck coefficient was found out ~ -91.65 μV/K.

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